Proc. Int. Conf. on Corrosion CONCORN '97
December 3-6, Mumbai, India

Effect of Mixed Cations on Phosphate Coating of Steel

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Abstract

Effect of variations in the constituents of phosphating baths having Zn^{2+}, Mn^{2+}, Ni^{2+} and Ca^{2+} on performance of produced coatings on steel surfaces, have been studied. It is observed that a bath having Zn + Mn + Ni as their phosphates and Ca as nitrate, provides excellent coating on the surface. Addition of urea (U), hexamine (HA), guanidine nitrate (GN) and nickel nitrate (NIN) provides different types of effects. HA doubles the rate of coating formation but produces a coarser and poorer corrosion resistant film. Thermal resistance, spot corrosion resistance, alkali resistance tests and immersion resistance tests have been performed to determine the characteristics of the coatings. Salt spray resistance (B 117) studies indicate that the phosphated surface having passivation treatment of **Phosave** (a trade name) provides an excellent improvement in controlling of appearance of brown rust on the surface. Electrochemical studies indicate that the produced coating is more resistant in saline environment than sulphurous acidic environments. SEM studies indicate that the addition of GN in phosphating baths has a strong influence in transforming the morphologies of phosphate crystal structure from coarse to finer one.

1. INTRODUCTION :

Zinc phosphate coatings on steel surfaces are applied to achieve conversion coatings of zinc and iron phosphate. These coatings provide good corrosion resistance, act as absorbent for lubricant in contact of lubricating agents and increase the life of dies, provide excellent base for the applications of paints and sometimes also used to harden the surface to achieve abrasion resistance. Out of these applications, the application of paints and coatings on phosphated surface is the most critically affected due to the variation in morphology of structure of phosphate layer. In recent years, attempts are being made to modify the coating structures by providing appropriate optimized treatments by incorporation of cations, surfactants and changing parameters of bath to achieve high degree of corrosion resistance (Salt spray and immersion tests), thermal resistance and alkali resistance[1-5]. Amongst the various types of cations, zinc in combination of Mn^{++} and Ni^{++} is reported to provide superior performance. However, the studies in our lab have shown that incorporation of Ca^{++} in the coating improves the performance to a great extent, especially in changing the morphology of structure of the coatings. The types of passivation treatments provided on the phosphated surface also affect the degree of corrosion resistance to a considerable extent. A Literature survey of last 10 years has shown that the details about such types of phosphatings are not reported in research papers. The Present work was undertaken to have a detailed investigation on the coating provided by a phosphating composition having Zn^{2+}, Mn^{2+}, Ni^{2+} and Ca^{2+} and also incorporation of some surfactants in the coating bath.

2. EXPERIMENTAL DETAILS :

2(a). Composition of substrate : Mild steel coupons having 0.15% C, 0.6% Mn, 0.055% S and 0.09% P were used as the substrate to provide coating. Reagent grade chemicals were used for the preparation of baths. The steel coupons of size 7.5 cm x 2.5 cm x 0.05 cm were cut and pickled in 10% HCl. The specimen were then exposed in phosphating bath maintained under different conditions.

2(b). Phosphating bath compositions and deposition of coatings :
Following are the compositions of baths chosen for the studies :

Table I : Compositions of phosphating baths.

Bath No.	Concentration of ingredients gms/litre			
	Zn phosphate	Ni phosphate	Mn phosphate	Ca nitrate
B1	20	00	20	20
B2	00	20	20	20
B3	20	20	20	20
B4	10	10	10	10

In all the cases, the pH of the bath was maintained at 3.5 by addition of appropriate amount of phosphoric acid. The experiments were performed in beakers keeping them in thermostatically controlled water baths. In each sets of experiments, 6 samples were tested simultaneously and average results were calculated. To determine the coating weight, the weight of samples were taken prior to and after phosphating. The final weights were taken after dissolving the phosphated specimen in 10% NaOH for 20 minutes.

2(c). Salt spray resistance tests : These tests were performed as per B 117. The observations were made after each 8 hours of exposure time .

2(d). Immersion tests : Immersion tests were performed by dipping the specimen in 3.5% NaCl solution at 30 ^{o}C. After 360 hours of exposure , the iron leached out in the solution was determined by titration method. Spot corrosion resistance tests were performed by making cross scratches on the painted panels (provided with 3 coats of acrylic paints and dried for 72 hours prior to giving scratch tests) and dipping in 5% NaCl + 0.5% $CuSO_4$ solution for 50 minutes. The corrosion of spots appeared on the surface were counted by visible observations.

2(e). Thermal resistance tests : In this test, the phosphated specimen were placed in oven at 100^{o}C for 10 minutes. The temperature was increased from 100 to 180^{o}C in 45 minutes. After this heat shock, the specimen were removed and kept in dessicator and cooled there. The weight changes were determined after 6 hours.

2(f). Alkali solubility tests : The phospnated surface was dipped in 0.1N NaOH for 60 minutes. The coupons were then removed and dried with hot air. Percentage coating weights left on the surface were recorded by loss in weight divided by the original weight of coating multiplied by 100.

2(g). Electrochemical studies : Electrochemical studies were performed by cutting the specimen of 1 cm^2 area from the phosphated panels. The edges of the panels were coated with acrylic paint. The tests specimen had stem of 5 cm length through which electrical contacts were made. Potentiodynamic polarization tests were run in 3.5% NaCl and in acidic distilled water (pH = 3.5 brought down by the addition of sulphuric acid). The specimen initially were put in the electrolyte to achieve a steady state open circuit potential. The polarization runs were then performed first starting the potential from negative potentials to positive potentials. The scan rate in all the cases was maintained at 100 mv/min, using a potentiodyne analyser (supplied by M/S Petrolyte Corporation, U.S.A.). All the potentials were measured against saturated calomel electrode (SCE).

3. RESULTS AND DISCUSSIONS :

Total acidity, free acidity, acid ratio values before and after phosphate treatments and coating weights are given in Table I.

Table II : Total acidity (TA), free acidity (FA), acid ratio (R), Coating weight (gms/m^2) in different baths.

Treatment time : 15 minutes
Total area phosphated : 0.03 m^2
Temperature of bath : 90 °C (B1, B2 and B3)
80 °C (B4 and B4 + additives)

Baths	Before experiment			After experiment			Iron loss gms/m^2	Coating w gms/m
	TA	FA	R	TA	FA	R		
B1	47.0	6.8	6.9	41.8	5.8	7.20	8.20	10.70
B2	46.0	7.1	6.5	42.4	5.0	8.5	15.60	52.74
B3	54.4	8.0	6.8	50.4	6.6	7.63	11.31	20.69
B4	21.8	3.9	5.6	19.6	3.6	5.5	3.03	9.38
B4 + HA	21.4	3.4	6.3	17.4	1.4	12.5	3.41	19.50
B4 + U	21.0	4.3	4.9	17.6	2.2	8.0	2.72	10.44
B4 + GN	22.2	4.0	5.5	18.2	2.4	7.50	3.01	10.80
B4 + NIN	22.4	4.6	4.87	17.6	2.4	7.33	2.81	9.08

(HA = Hexamine, U = Urea, GN = Guanidine nitrate, NIN = Nickel nitrate. All added at the concentration of 0.05%).

The above Table shows that baths B1, B2 and B3 provide very high weight of coating and also cause severe dissolution of iron. These baths were, therefore, not further investigated. Bath B4, which was prepared by mixing of Zn, Mn, Ni and Ca was taken as an ideal bath as the acid ratio of the bath before and after phosphating was the same. This type of baths are considered ideal from stability point of view. Addition of HA in this bath has a strong accelerating effect on the coating formation. The coating weight has almost doubled in this case, in comparison to the blank and other additives. Iron dissolution in presence of HA is also increased to some extent but not in ratio of increase in the coating weight. A careful examination of the results indicate that in the presence of all the additives, the change in total acidity of the bath after experiments, is of the order of 4 pointage as compared to only 2 in blank (B4) solution. The deposition of coating weight in all the cases except HA is of the order of 9-10 gm/m^2. These observations indicate that HA helps in converting of maximum soluble metal phosphates (present in the form of total acidity) into insoluble phosphates who crystallize on the steel surface. Very limited amount is wasted in the form of sludge. In contrast to this,the other additives convert a greater fraction of phosphates into insoluble phosphates in the form of sludge. The greatest disadvantage associated with HA however, is its tendency to drastically increase the acid ratio value of bath after the coating treatment which is 12.5 against its original (prior to coating) value of 6.3. The other additives change the acid ratio values of the order of 3 only. A negligible effect in acid ratio is noted for the bath having no additive.

Salt spray resistance tests on the performance of different types of coatings and effect of passivation treatment have been incorporated in Table III.

Table III : Effect of salt spray on corrosion resistance of unpassivated and passivated phosphated surface. Temp = 80 °C, Time of treatment = 15 minutes

Baths	Hours of exposure$							
	Unpassivated				Passivated NML-Phosave			
	24	48	72	144	24	48	72	144
B4	100	--	--	--	OK	OK	5	40
B4 + HA	25	50	--	--	OK	50	60	100
B4 + U	100	--	--	--	OK	5	20	25
B4 + GN	OK	5	20	80	OK	OK	5	10
B4 + NIN	OK	5	50	100	OK	OK	10	10

$(The numbers indicate the percentage of rusting appeared on the surface)

The above table shows that the baths B4 and,B4 having urea exhibit extremely poor salt spray resistance under unpassivated conditions and the whole surface is rusted within 24 hours of exposure. The baths having GN and NIN, however, provide superior performance and almost no attack is noted upto 48 hours of exposure. A drastic improvement is noted when the phosphated surfaces were passivated in 2% of **NML-Phosave** (a passivator having Cr^{6+}, Cr^{3+} and organic chemicals). The baths B4 and B4+U exhibit salt spray resistance of over 72 hours under passivated conditions compared to hardly 8 hours in the conditions of unpassivated surface.GN and NIN provided further improved life of 144 hours under passivated conditions. These improvements were achieved clearly due to the blocking effects of **Phosave** on the pores existing in phosphated layers (The phosphated layers produced by B4, B4 + U had very bigger size of crystals and the surface had appreciable amount of porosity, as discussed later).

The change in open circuit potential of unpassivated phosphated surface with passage of time is shown in figure 1. In all the cases, it is noted that the potential shifts in -ve direction with the passage of time and stabilize almost after one hour. The trend in case of passivated surface had also been the same except that the stabilized potential values varied considerably in comparision to the passivated potential. These potentials are shown in Table IV.

Table IV : Stabilized potential (mv) and time required to achieve stabilized values for unpassivated and passivated surfaces. Electrolyte = 3.5% NaCl.

Baths	Unpassivated		Passivated	
	Stabilized potential	Time (minutes)	Stabilized potential	Time (minutes)
B4	-606	105	-572	110
B4 + HA	-606	105	-610	110
B4 + U	-606	105	-580	105
B4 + GN	-606	105	-575	85
B4 + NIN	-606	105	-600	75

In normal NaCl electrolyte, oxygen reduction reaction i.e.,

$$O_2 + 2H_2O + 4e^- \text{------>} 4OH^- \quad \text{.....(i)}$$

is the cathodic reaction. A shift of potential in active direction indicates the polarization of this reaction. A faster rate of polarization is observed in passivated surface of phosphate coating provided in the presence of GN and NIN, as evident from the time required to stabilize the potential. This is attributed to the blocking effect of **Phosave** of pores of phosphate layer with increase in pH at the interface, as a result of OH^- ions generated by the reaction (i).

The results showing the effect of type of phosphate coating on thermal resistance (TR), corrosion resistance (CR), alkali resistance (AR) and immersion resistance (IR) are tabulated in table V.

Table V : TR, CR and AR for various types of coatings.

Baths	TR	CR	AR	I R Iron dissolved
	% wt. loss	%rusted spot	% wt of coating left	mg / cm square
B4	10.24	7	83.76	1.21
B4 + HA	10.70	14	92.00	1.32
B4 + U	10.04	29	87.31	1.06
B4 + GN	9.83	38	88.81	0.85
B4 + NIN	10.20	41	88.83	0.89

Phosphated surfaces are exposed to thermal treatments during the baking of the paints applied over the surfaces. This baking is carried out at about 180°C in heating ovens. During this baking process, the water of crystallization present in the coating is lost and results in changing of microstructure of coating. The corrosion resistance and adhesion properties of the phosphate coating is adversely affected due to the loss of water of crystallization. Calculation of percentage of water in coating weight [$Zn_3(PO_4)_2 . 4H_2O + FeZn_2(PO_4)_2 . 4H_2O$] shows that about 20% of weight of coating is the water of crystallization. For a good coating, the loss of water should not go beyond 10% . A pure Zinc phosphate coating exhibits loss of water > 15%. A tricationic phosphating , however, resists the dehydration of coating during the baking process. This is evident from the above table where the TR values in all the compositions are almost of the order of the 10% loss of coating weight. Appearance of the rusted spots on cross hatched surface is the lowest in the bath having no additive. Alkali resistance of coating is also lowest in the case of blank bath having no additive. This is best in case of the bath having HA as the additive.

Immersion resistance of coating is best achieved in the bath having GN (0.85 mg/cm^2 of iron leached out from the coating/substrate) whereas it is worst for the blank solution + HA (1.32 mg/cm^2). This observation is totally in contrast with the observations noted for alkali resistance. Where B4 + HA provides higher value of coating weight left on the surface (92%).

Potentiodynamic polarization plots for the phosphate coatings produced in bath B4 (Zn+Mn+Ni) and having passivation and no passivation treatments are shown in figure 2. These plots have been drawn in 3.5% NaCl and in acidic distilled water (pH=3.5) brought down by the addition of sulphuric acid. These studies were performed to study the effect of saline environments

(experienced in coastal areas) and sulphurous environment (experienced in industrial areas) on deterioration of phophate coatings. It is observed from the figure that the corrosion rate in acidic environments, where hydrogen evolution is the cathodic reaction, is more (about 100 times) than in chloride environments, where aggressive ion is chloride and oxygen reduction is the cathodic reaction. In both the cases, the passivation treatment provided by **Phosave** has a pronounced effect on the dissolution of phosphate (anodic polarization) and the cathodic reaction. Passivation effect is more pronounced on the cathodic reduction of oxygen.

Microstructures of phosphated surface produced in the presence of B4 bath and having GN and HA are shown in figures 3 (a), (b) and (c) respectively. It is evident from the microphotographs that in the absence of any additive, the bath B4 produces coarse and fine crystals of phosphate. EDX analysis of these cystals exhibited that the majority of the constituent was zinc followed by iron and manganese phosphates. Trace amount of nickel was also noted. It further reveals that the growth of crystal was not uniform. When GN was present in the same bath, very fine and uniform types of crystals were produced (figure 3-(b)). Addition of HA, on the other hand, produced very coarse structures (figure 3-(c)). These structures have strongly influenced the corrosion resistance properties of the coatings produced on the surface.

4. CONCLUSIONS :

(i) The phosphate coatings produced by Zn+Mn+Ni phosphate baths provide excellent resistance towards thermal resistance, corrosion resistance and alkali resistance.

(ii) Addition of HA in the bath strongly enhances the coating weight formation but has adverse effects on other properties.

(iii) Presence of guanidine nitrate (GN) in the bath has a strong positive influence on corrosion resistance properties of tricationic phosphating.

(iv) Passivation of phosphated surface using NML-**Phosave** strongly enhances the protective properties of the coatings. This improvement is reflected in salt spray, immersion and other tests.

(v) The phosphate layer produced is more resistant in saline environment than in sulphurous acidic environments.

(vi) Microstructures reveal that GN addition in the bath helps in producing smaller and uniform crystals of phosphates.

5. ACKNOWLEDGEMENTS :

The authors are thankful to the Director, NML, Jamshedpur for his constant encouragements in accomplishing this work.

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